

Structure of Precipitated Silica

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Introduction

Reinforcing fillers are used to enhance the mechanical properties of polymers in general and elastomers in particular. For decades carbon black has been the dominant material used for tire reinforcement. Recently, however, many tire manufacturers have incorporated colloidal silica, usually in combination with carbon black, to improve the rolling resistance with little or no sacrifice in traction or wear. It is of interest, therefore, to determine the structure of these two materials in order to trace performance characteristics to the physical characteristic of the filler colloids.

The complex structure (Figure 1) consisting of primary particles aggregated into micron-sized clusters is known to be necessary for effective reinforcement, but there is little consensus on why such a structure is necessary. Part of the motivation of our work was to search for common structural features in both the silica and carbon systems that might illuminate this issue.¹

Characterization of aggregated structures is a major challenge since these materials show distinct structural features over many decades in length scale, the signature of the complex growth processes active during synthesis. Figure 1 shows schematically the processes that are believed to be active during synthesis along with the structural features resulting from these processes. The region of particular interest in the small-angle profile lies between $0.00001 < q \text{ (}\text{\AA}^{-1}\text{)} < 0.1$, the range covered by the UNICAT USAXS instrument.

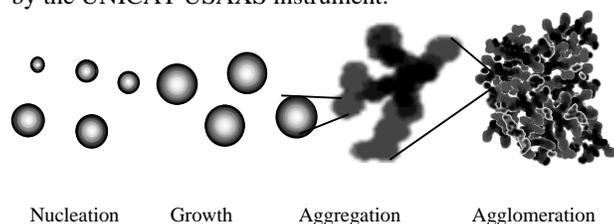


Figure 1. Stages of colloidal growth of precipitated silica.

We have synthesized several kinds of precipitated silica by using different protocols. Also, several kinds of interface-modified silica were synthesized by using different modifiers such as dichlorodimethylsilane. Our goal is to control both the structure of the aggregate/agglomerate and to optimize the structure for effective reinforcement. In addition, we hope that we can improve dispersability in the final dried product as a result of interfacial modification during the synthesis.

In order to make quantitative measurement we need the absolute scattered intensity. This requirement means that we must know the density of our powder samples, a parameter that is difficult to establish for very thin powder samples. We tried making powder monoliths using agar as a binding agent. Even for the thinnest sample, however, (1 mm) we found multiple scattering, forcing us to use a dusting of powder on a tape as our final sample configuration. As a result, we were unable to achieve

our goal of absolute measurements. Subsequent attempts to achieve thin, low-density monoliths have proven unsuccessful.

Results

Figure 2 compares the USAX profiles for precipitated silica prepared by three protocols. Two follow patented procedures²

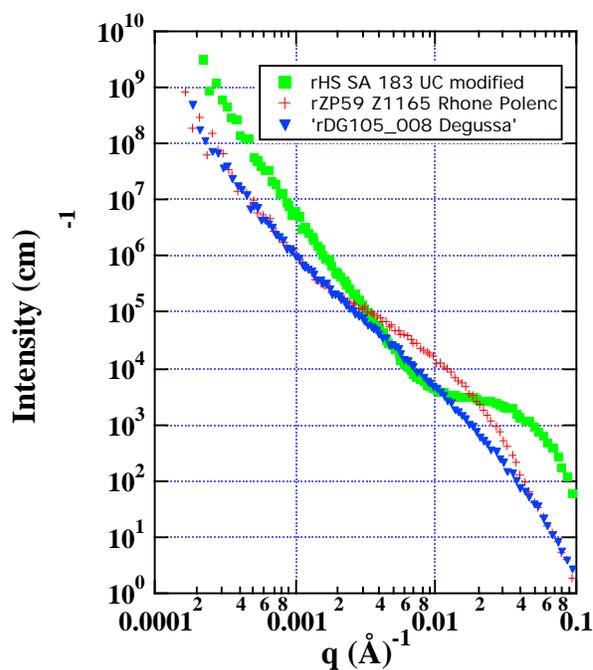


Figure 2. Scattering profiles for three precipitated silicas.

while the third is prepared by one of our protocols in which the neutralization of the original water-glass solution is carried out so as to minimize the ionic strength of the reacting solution.

Discussion

The data in figure 2 show that drastic changes of structure can be achieved by rather minor changes in protocol. Compared to the patented protocols, our primary particles are substantially smaller. More interesting however is that the profile is flat in the region that is sensitive to the “aggregate” in Figure 1. It appears that either normal fractal aggregation is completely suppressed or that the aggregates are so interpenetrated in the final agglomerate as to be invisible to USAXS³.

Acknowledgments

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